Vibrationally Resolved O 1s Excitations in CO and NO

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INTRODUCTION

Recent improvements in synchrotron light sources and beamlines have made it possible resolving the vibrational fine-structure of numerous core-excited molecules using photon energies up to ≅ 400 eV (e.g. Si $2p^{-1}$, C $1s^{-1}$, N $1s^{-1}$) [see e.g. 1-3]. However, at even higher photon energies, the instrumental resolution of monochromators was not sufficient until very recently to obtain full information on the vibrational fine structure. For example, earlier high-resolution photoabsorption measurements of CO and NO below the O 1s threshold with a resolution ΔE≅120 meV using the SX700/II monochromator at BESSY/Berlin, only partially revealed the vibrational fine structure [1,2].

We report here on new photoabsorption measurements of CO and NO below the O 1s ionization threshold with substantially improved resolution (ΔE ≅ 65 meV), resulting in completely resolved vibrational fine structures. The new spectra allowed Franck-Condon analyses, providing information on the potential-energy surfaces of the core-excited states.

EXPERIMENT

The measurements were performed at BL 7.0.1 at the ALS/Berkeley using the built-in photoionization cell that consists of two parallel plates with an active length of 20 cm for collecting the charged particles. The photoionization cell was separated from the UHV of the monochromator by an 1000-Å thick Al (1% Si) window; it was filled with 10 to 50 μbar of CO and NO. The spectra were measured with 8-μm entrance and exit slits, resulting in a spectral resolution of ΔE ≅ 65 meV.

RESULTS AND DISCUSSION

O 1s excitations in CO

The photoionization spectrum of the O $1s^{-1}\pi^*$ excitation in CO, with completely resolved vibrational fine structure, is shown in Fig. 1. This improved spectrum allowed for the first time to perform a Franck-Condon analysis of this excitation, resulting in an increase of the equilibrium distance from r"=1.1283 Å in the electronic ground state to r'=1.291(3) Å in the core-excited state. In addition, a decrease of the vibrational energy from $\hbar\omega$"=269.025 meV in the ground state to $\hbar\omega$'=166(1) meV in the core-excited state as well as a slight increase of the anharmonicity from $x\hbar\omega$"=1.647 meV to $x\hbar\omega$'=1.8(1) meV were derived. We obtain a decrease of the dissociation energy from D_e"=11.0 eV in the ground state to D_e'=3.9 eV in the core-excited state according to $D_e=(\hbar\omega)^2/4x\hbar\omega$. The resulting parameters of the core-excited state agree fairly well with calculations of Correira et al. [4], with $\hbar\omega$'=176.8 meV, $x\hbar\omega$'=2.3 meV, and r'=1.280 Å. The increase of the equilibrium distance as well as the decrease of the

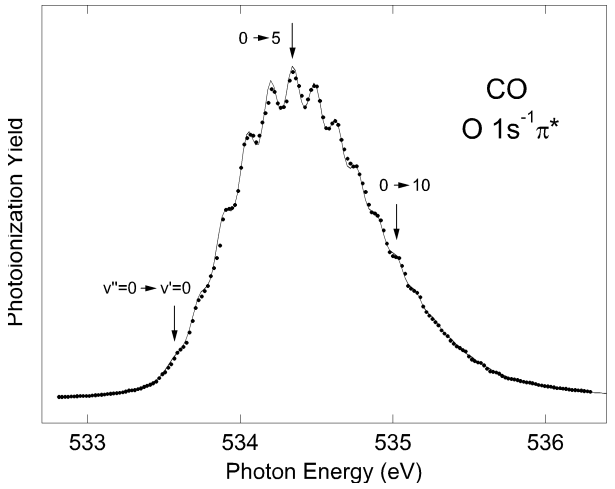

Fig. 1: O $1s^{-1}\pi^*$ excitation in CO. The solid line through the data points represents the results of a Franck-Condon analysis.

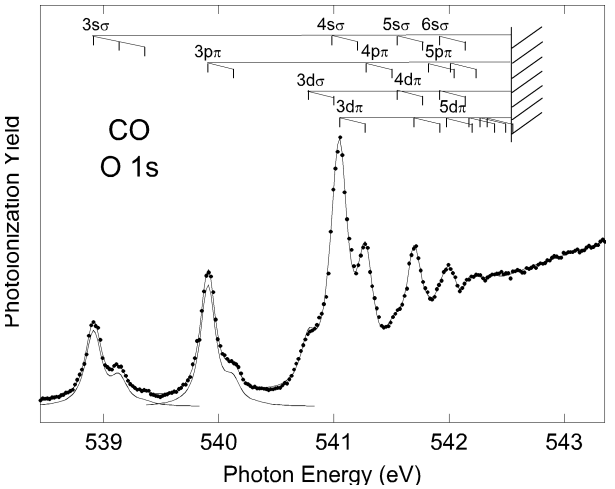

Fig. 2: Rydberg region of CO below the O 1s ionization threshold. The solid line through the data points represents the results of a fit analysis. The subspectra below the spectrum represent the results of a Franck-Condon analysis of the Rydberg states O $1s^{-1}3s\sigma$ and O $1s^{-1}3p\pi$. The assignment is given by the vertical bar diagrams above the spectrum. The first bar for each resonance represents the v''=0 → v'=0 excitation, while the other bars represent higher vibrational substates.

vibrational energy and the dissociation energy upon excitation can readily be understood on the basis of excitation into an antibonding π* orbital.

The Rydberg region of the O 1s core excitation spectrum of CO is shown in Fig. 2 together with the assignments. For the two lowest Rydberg states at hν≅539 and 540 eV, a Franck-Condon analysis has been performed, resulting in an increase of the equilibrium distance from r''=1.1283 Å in the electronic ground state to r'=1.169(2) Å [r'=1.158(2) Å] as well as a decrease of the vibrational energies from $\hbar\omega''$=269.025 meV to $\hbar\omega'$=223(3) meV [$\hbar\omega'$=223(3) meV] in the O $1s^{-1}3s\sigma$ [O $1s^{-1}3p\pi$] Rydberg state upon excitation. The vibrational-energy splitting and the intensity ratios of vibrational substates of the O $1s^{-1}3p\pi$ Rydberg state is transferred to the higher Rydberg states in order to perform a fit analysis. This analysis results in the assignment given in Fig. 2 with four Rydberg series and quantum defects of δ=1.06 (nsσ series), δ=0.73 (npπ), δ=0.22 (ndσ), and δ= –0.02 (ndπ). These results differ from earlier experiments, where only three Rydberg series (nsσ, npπ, ndσ) with doubtful intensity ratios were observed.

O 1s excitations in NO

NO has one additional electron as compared to CO, which is located in the antibonding π* orbital. Due to the singly occupied π* orbital, NO is called an open-shell molecule. Upon core excitation, the single π* electron can interact with the core hole and the excited electron, leading to new effects as compared to CO, e.g. three substates of the O 1s→π* excitation and two O $1s^{-1}$ ionization thresholds are observed. A more detailed discussion of this interaction and its influence on the spectral features is given e.g. by Wight and Brion [5].

Fig. 3 shows the O $1s^2\pi^*\rightarrow$O $1s(\pi^*)^2$ excitations in NO, which are represented by three substates ($^2\Sigma^-$, $^2\Delta$, $^2\Sigma^+$) due to the interaction between the core hole and the two π* electrons.

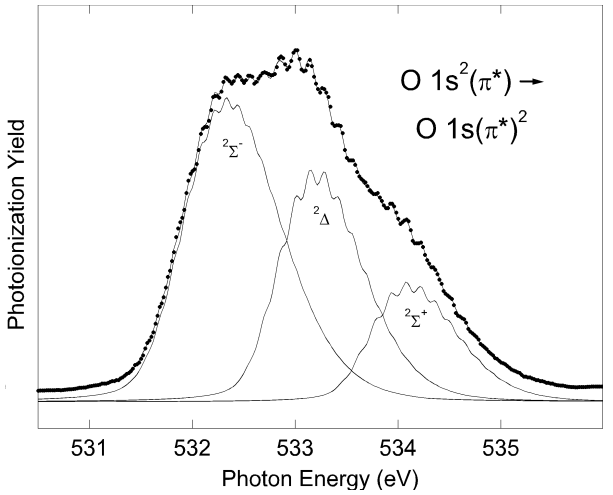

Fig. 3: The O $1s^{-1}\pi^*$ excitation in NO. The solid line through the data points represents the result of a Franck-Condon analysis. The three subspectra describe the three substates.

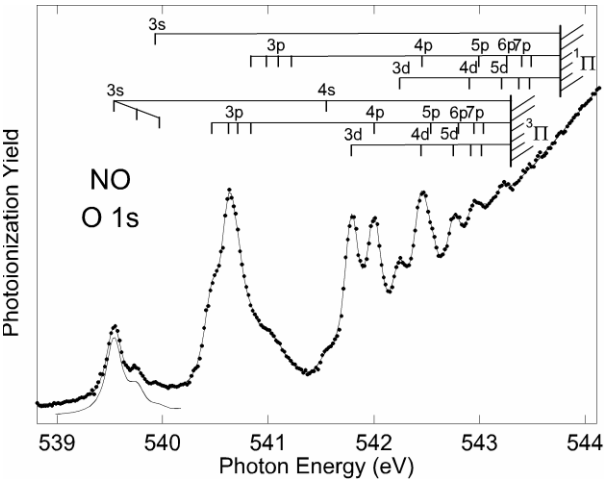

Fig. 4: The Rydberg region of NO below the O 1s ionization threshold. The solid line through the data points represents the result of a fit analysis. The subspectrum below the spectrum describes the result of a Franck-Condon analysis of the O $1s^{-1}3s\sigma$ Rydberg state. The assignments are given by the vertical bar diagrams above the spectrum. The first bar for the 3s resonance represents the v"=0→ v'=0 excitation, while the other bars describe higher vibrational substates.

Contrary to previous high-resolution photoabsorption measurements [2], the vibrational fine structure of the substates are completely resolved and allow a Franck-Condon analysis. The results of this analysis are represented by the solid line through the data points and the three subspectra. The values obtained for the equilibrium distances r' and the vibrational energies $\hbar\omega'$ for the core-excited states are summarized in Table 1. For comparison, the theoretical results obtained by Fink [6] are also given. It can be seen that for all three substates the vibrational energies decrease from $\hbar\omega$"=235.9 meV to $\hbar\omega' \cong 150$ meV and the equilibrium distances increase form r"=1.151 Å to r'≅1.32 Å. Again, this can be understood by excitation into an antibonding orbital. A detailed comparison of the equilibrium distances and the vibrational energies with the values given by Fink reveals good agreement.

The Rydberg region of NO below the O 1s ionization threshold is shown in Fig. 4. The vertical-bar diagrams above the spectrum represent the assignments of the Rydberg states converging towards the O 1s ionization thresholds $^3\Pi$ and $^1\Pi$. This splitting is due to an interaction between the O 1s core hole and the π* electron. Three Rydberg series with quantum

Table 1: Results of the Franck-Condon analysis of the O $1s^{-1}\pi^*$ excitations in NO. Given are the vibrational energies $\hbar\omega$ and the equilibrium distances r for the electronic ground state (g.s.) the the three core-excited states $^2\Sigma^-$, $^2\Delta$, and $^2\Sigma^+$. For comparison, the theoretical results from Fink [5] are also given.

	$\hbar\omega$ (meV)		r (Å)	
	this work	Fink [6]	this work	Fink [6]
g.s.	235.9		1.151	
$^2\Sigma^-$	137(3)	139	1.348(3)	1.339
$^2\Delta$	154(3)	159	1.311(3)	1.295
$^2\Sigma^+$	157(3)	162	1.306(3)	1.290

defects of δ=1.10 (ns Rydberg series), δ=0.75 (np), and δ=0.00 (nd) are identified.

The vibrational fine structure of the O $1s^{-1}(^3\Pi)3s$ Rydberg state is clearly resolved for the first time and Franck-Condon analysis are performed resulting in a decrease of the vibrational energy from $\hbar\omega''$=235.9 meV to $\hbar\omega'$=218(2) meV and a increase of the equilibrium distances form r''=1.151 Å to r'=1.190(2) Å. The improved spectrum allowed to determine the $^3\Pi$ - $^1\Pi$ splitting of the O 1s ionization threshold to $\Delta I_p = I_p(^3\Pi) - I_p(^1\Pi)$=456(15) meV. This value is more precise and significantly smaller than previous results of 510 meV [2] and 550 meV [7].

CONCLUSIONS

The significantly improved energy resolution of the present work allows resolution of the complete vibrational fine-structure and Franck-Condon analyses, resulting in detailed information on the potential-energy surfaces, i.e. on the vibrational energies and equilibrium distances of molecules after O 1s core excitations.

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